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Procedia Engineering 26 (2011) 1019 – 1025

Procedia Engineering

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First International Symposium on Mine Safety Science and Engineering

Experimental Study on Thermal Decomposition and Kinetics of Mine Timber in Air Atmosphere

Peng Chen[a*], Zihua Liu[a], Jinhua Sun[b]

[a] *School of Resources and Safety Engineering, China University of Mining and Technology, Beijing, 100083, China*
[b] *State Key Laboratory of Fire Science, University of Science and Technology of China, Hefei，230026, China*

Abstract

Mine fires are the major disasters in process of coal production, and the mine timbers that can lead to fires are still significant hazard sources. For timber fires, thermal decomposition provides the necessary fuels for combustion in gas phase. To investigate the thermal decomposition kinetics of the mine timber, a typical timber is taken as experimental sample in this paper. TG and DTG techniques are carried out at different heating rates. Physical, chemical and thermal effect changes are analyzed according to the pyrolysis process. As temperature increases, the timber pyrolysis process shows four phases with varied physicochemical properties and heat effect. Two-phase and first-order thermal kinetic models for the decomposition of mine timbers are advanced, and the kinetic parameters are obtained. Those researches are benefit to understanding the ignition mechanism and flame spreading of timber fires in coal mines.

Selection and/or peer-review under responsibility of China Academy of Safety Science and Technology, China University of Mining and Technology(Beijing), McGill University and University of Wollongong.

Keywords: Coal mine fires; mine timber; thermal decomposition; dynamic model

1. Introduction

Mine fires are the major disasters in process of coal production. With the improvement of mechanization and supporting conditions in coal production, the timbers employed as supporting decline. However, the absolute amount of timbers used in coal mines, especially in small scale mines, is still substantial. Therefore timber fires are still hazard sources in coal mine. To date, lots of documents [1-9] are generated on mine timber fires. For example, Chen Yuanping etc.[1] compared PVC conveyor belt with timber on fire performance, heat release properties, smoke toxicity and reduction of light of CR by

* Corresponding author. Tel.: +86-10-62339160; fax: +86-10-62339160.
E-mail address: chenpeng@cumtb.edu.cn.

doi:10.1016/j.proeng.2011.11.2269

using cone calorimeter. Pan Dexiang etc.[2] studied combustion characteristics of the fire-retardant conveyor belts, hairdryers and pine timber under the radiation of 35 Kilowatt per square meter and obtained the combustion characteristic parameters of these materials. For the mine timber fires, two processes should be analyzed. One is the process of thermal decomposition that provides the necessary fuels and another is the combustion in gas phase. The heat release rate of timber can be simulated by the product of produce fuel rate and heat of combustion, so the thermal decomposition rate determines the heat energy in the burning triangle. In a sense, the behavior of thermal decomposition of timber plays a key role both in ignition and fire spreading process. Inspection on the thermal decomposition behavior and rule of timber can promote understanding of the mechanism of mine timber fire and establishing the timber fire model and the fire spread model require more works on the thermal decomposition process. So far, few researches are reported on the analysis of thermal decomposition kinetics of mine timber under air atmosphere. In this paper, thermal decomposition characteristics of timber and its kinetics are studied, and the thermal decomposition kinetics model under air atmosphere is advanced based on the experimental results.

Nomenclature

a	weight loss percentage
A	pre-exponential factor (min^{-1})
R	gas constant
β	heating rate (℃/min)
E	activation energy (KJ/mol)
i	weight loss stages
T	initial temperature (K)
T1, T2	peak temperature in DTG
a_i	weight loss rate in each stage
W	weight loss
∝	final stage

2. Experimental apparatus and methods

TA-50 thermal analyzer made in Japan Shimadzu Company is used. In the Experiment, the programmed temperature ranges are from 25℃ to 800℃ at heating rates of 5℃/min -1, 10℃/min -1, 15℃/min-1 and 20℃/min -1 respectively. The experimental samples of carbonized materials are homogenous dry timber. To reduce physical effects such as heat transfer and mass transfer, samples should be fully grinded and filtered with a 30 meshes sieve. In order to reduce the impact of the second gas-solid reactions and ignore the mass diffusion factor, the sample weight must be less than 4mg.

3. Experimental results and analysis

3.1. Experimental results

TG and DTG curves are shown in figure 1. The temperature increase of the samples depends on the heat transfer through the pot. So the temperature difference occurs between the heating stove and samples. For the change of enthalpy caused by such factors as character, size and physicochemical change of the samples, the temperature gradient comes into being. As shown in TG curves, with the increase of heating rate, the start-stop temperatures in each stage move slightly to high temperature zones in figure 1.

The DTG curves of the timber decomposition bear the accordant evolvement trend under varied heating rates. As shown in DTG curves, with the increase of heating rate, the start-stop temperatures move slightly to high temperature zones. The reaction time becomes shorter and the extent of reaction alters lower, as the heating rates rise. This heating delay is caused by such factors as temperature gradient between the measuring point and sample. For small timber particles, two separate peaks are induced due to the cellulose and the hemi cellulose thermal decomposition under varied heating rates.

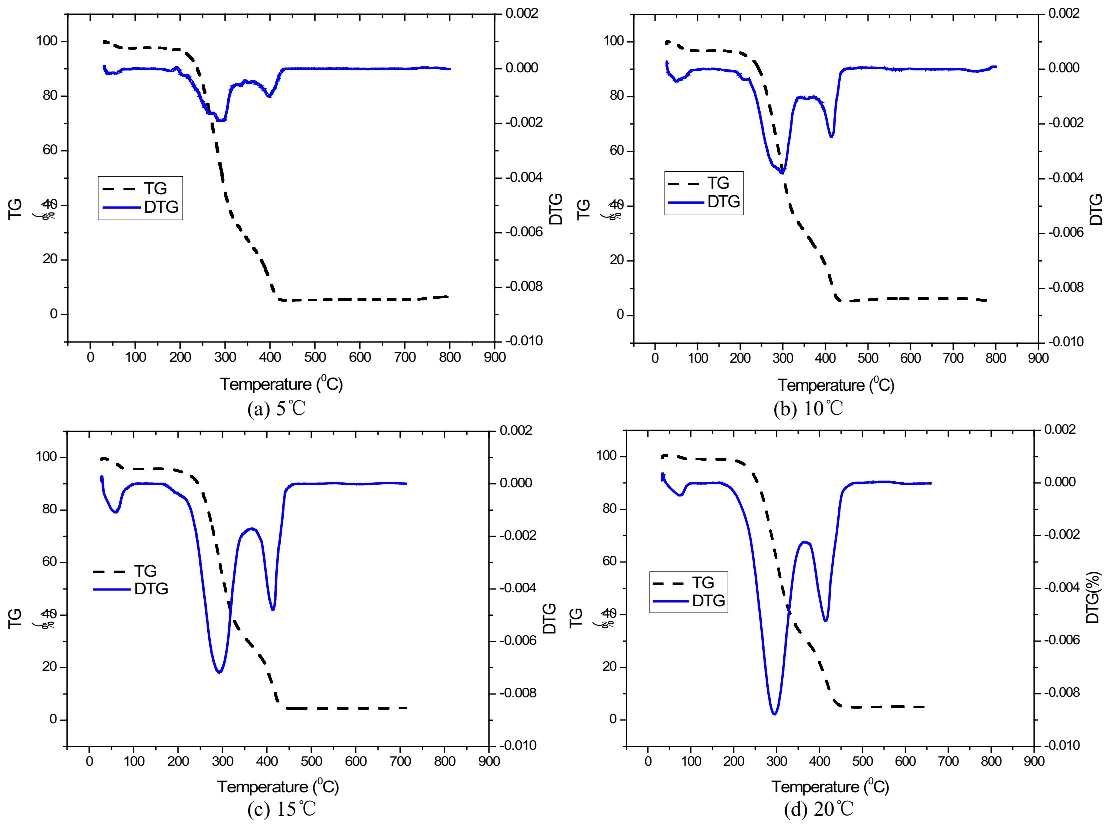

Figure 1 TG and DTG diagram of timber thermal decomposition at different heating rates under air atmosphere.

3.2. Thermal decomposition process of mine timber under air atmosphere

The features of thermal decomposition include such thermal behaviors as endothermic or exothermic, mass loss, release of volatiles, carbon layer collected and the other related properties respectively. For timber, the thermal decomposition comprise of two processes. One is chemical thermal degradation and another is chemical decomposition under higher temperature. In the process of thermal degradation a few chemical bonds in material structure are broken while few changes happen in the structure and property after heated. At a higher temperature thermal decomposition occurs. In the process of thermal decomposition the chemical bonds are broken and large scale volatile gases are generated and then liquids (tar) and carbonized residue are left. So physical phases and chemical properties of the mine timber change are basic. For timber, the thermal degradation occurs under both high temperature (>300℃) and lower temperature (<300℃), and figure 2 shows the thermal decomposition processes.

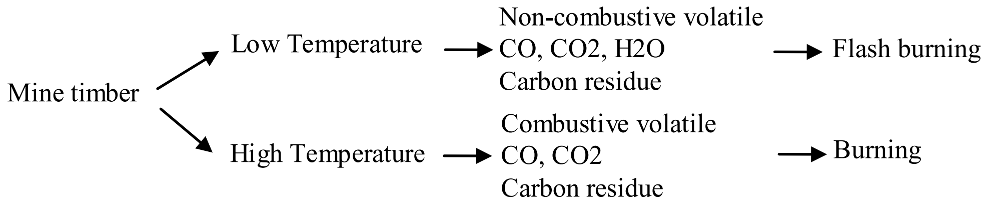

Figure 2 Schematic diagram of timber thermal decomposition

According to the TG and DTG curves the characteristic temperature curve at different heating rates can be obtained under air atmosphere. The results are shown in Table1. Under air atmosphere the weight loss characteristics of most biomasses are similar. When temperature is from 50℃ to 110℃, the sample will loss moisture content and the lost weight will amount to 4% to 6% of the initially total weight. Then the weight loss becomes smooth. The second process of weight loss will start at about 220℃ and accelerate from 280℃ to 370℃. The main stage of weight loss occurs from 230℃ to 420℃, during which it will take almost 80% contributing to the total weight loss. As the temperature reaches to 420℃, the sample weight loss stabilizes and the residues are solid cokes or indecomposable ashes. The three-step process of weight loss is corresponding to the three peaks in the DTG curve respectively. The first peak is small and not the main weight loss stage due to moisture evaporation. There is a significant turning point in the TG curve that divides the major weight loss process into two stages. The two higher peaks in the DTG curve respectively correspond to the maximum weight loss rates. For this phenomenon, Bilbao[7] suggests that the two-step process of weight loss correspond to thermal decompositions of the two main components. Component 1 is mixed with hemi cellulose and cellulose while component 2 is mainly composed by lignin. The two components decompose at different temperatures.

Table 1 Characteristic temperature at different heating rates

Heating rates	**Characteristic temperature of TG (℃)**			**Characteristic temperature of DTG(℃)**	
℃/min	$T_{5\%}$	$T_{60\%}$	$T_{90\%}$	T_1	T_2
5	218.8	283.1	405.8	289.03	389.21
10	213.6	291.4	418.1	296.17	413.62
15	200	294.2	421.2	293.76	414.91
20	239.4	301.3	425.6	294.01	415.34

3.3. Kinetics analysis of mine timber thermal decomposition

Thermal decomposition of solid carbonized materials can be expressed as the following reaction process [3, 4, 5]:

A (Solid) →B(Solid) + C(Gas)

Carbonized material A produces a solid phase B and combustible gas C if being heated. The reaction is usually assumed to be irreversible because the airflow used in the experiment will take away the volatile gases produced in the reaction.

Integral form of the dynamic equations can be advanced according to the characteristic equations of weight loss and the Arrhenius equation. Combined with the differential form of dynamic equations[10], the timber kinetic equation can be given as follows:

$$g(a) = \frac{A}{\beta}\int_{T_0}^{T} \exp(-E/RT)dT \qquad (1)$$

Here α can be expressed as

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty} \qquad (2)$$

Coats and Redfern [10] solved the integral equation of equation 1 as follows:

$$\ln\left[\frac{g(a)}{T^2}\right] = \ln\left\{\frac{AR}{\beta E}\left[1-\frac{2RT}{E}\right]\right\} - \frac{E}{RT} \qquad (3)$$

For 2RT/E<<1, if the form of $g(a)$ is correct, the curve of $\ln\left[g(a)/T^2\right]$ plots with 1/T should be a straight line, whose rate of slope is –E/R. The intercept of this straight line includes the frequency factor A. When $g(a)$ is determined, the activation energy E and the frequency factor A can be obtained from the rate of slope and intercept described above. The reaction mode $g(a)$ can be referred to reference [10].

The weight loss curves of carbonized solid combustible materials under air atmosphere can be divided into two stages, so the mass loss processes could be taken as two independent reactions. The formula 1 can be used in the two ranges respectively. The timber thermal decomposition is a very complex chemical reaction process which contains not only the hemi cellulose, cellulose and lignin decomposition but also many other reactions. For effects of these materials' reaction, the weight loss curves do not have one strict platform. As a result the point that corresponds to the end of a reaction and the start of the next reaction will not be clearly identified. Generally, the absolute minimum point in the DTG curves is taken as the dividing point of the two weight loss stages. The rate equations of weight loss in each stage can be shown as follows:

$$\alpha i = \frac{W_{i0} - W}{W_{i0} - W_{i\infty}} \qquad (4)$$

Based on experimental data shown in figure 1, the equation 1 can be solved and the two-phase dynamic models can be obtained. Figure3 and Figure 4 show comparisons of different models in the two thermal decomposition stages. It can be seen that the curve $\ln\left[g(a)/T^2\right]$ plots with 1/T corresponding to the second and the third model is sunken while to the zero-order model is concave, only the curve of the first-order reaction model is a basically straight line. Therefore it can be determined that the apparent reactions of the two stages are the first-order reactions.

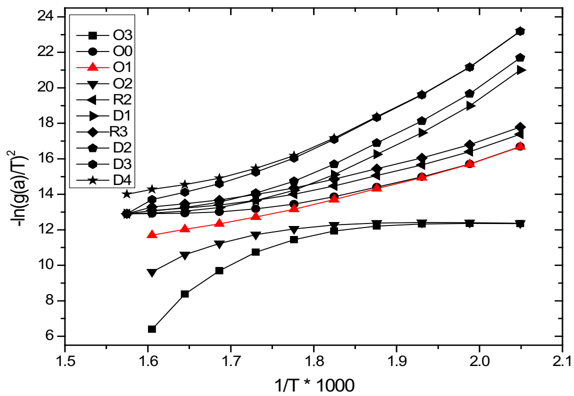

Figure3 Comparison of different models in the first thermal decomposition stage

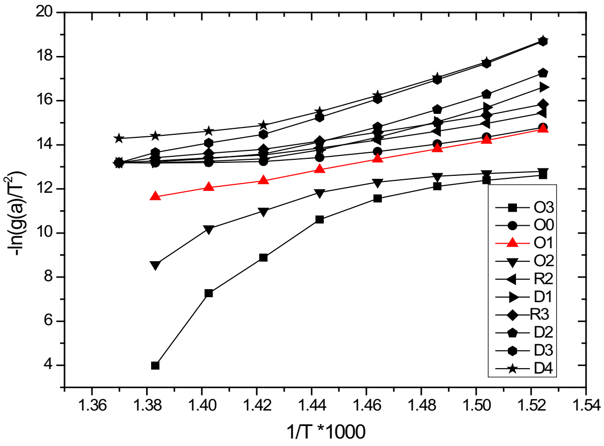

Figure 4 Comparison of different models in the second thermal decomposition stage

According to the first-order reaction model of the two-component phases, the kinetic parameters of thermal decomposition under air atmosphere can be calculated, as shown in Table 2.

Table 2 Kinetic parameters of mine timber thermal decomposition under air atmosphere

Stages	Temperature ranges of weight loss(℃)	Activation energy(KJ/mol)	Frequency factor A(s^{-1})
1	210—370	106.33	1.38E+06
2	370—430	175.48	3.42E+05

4. Conclusions

The thermal decomposition kinetics of mine timber has been investigated. Thermal decomposition kinetic models are advanced, and the corresponding kinetic parameters are obtained. Those help to understand the ignition mechanism and flame spreading in mine fires. The following conclusions are obtained:

With heating rates increasing, the reaction time is reduced and the start-stop characteristic temperatures in TG and DTG curves move to a higher temperature zones.

At air atmosphere, the thermal weight loss mainly goes through two stages with temperature increasing. According to the TG and DTG curves, the temperature of main zone of mass loss is from 230℃ to 420℃.

Two-phase and first-order thermal kinetic models for the decomposition of mine timbers are advanced. The relevant activation energy E is 106.33KJ/mol and 175.48KJ/mol and the frequency factor A equals to 1.38E+06s-1 and 3.42E+05s-1 corresponding to the two weight loss temperature ranges respectively.

Acknowledgements

This work was carried out and funded under university scientific research plan projects in Xingjian Uygur Autonomous Region (XJEDU2008141) and Open project in State Key Laboratory Fire Science(HZ2007-KF05).

References

[1] Wang Lei, Ji Jingwei, Cheng Yuanping, Gao Yufei,Experimental and numerical simulation research on burning characteristics of common combustible materials. Journal of China University of Mining & Technology; 2006, Vol.35(6), pp.732-736.(in Chinese)

[2]Pan Dexiang, Wang Yuhuai, Ma Shangquan, Yang Shousheng, Shu Zhongjun. Experimental research on combustion features of mine conveyor belt, ventilation tube and mine timber. Coal Science and Technology; 2005, Vol.33(7), pp.52-54.(in Chinese)

[3]Chenpeng. Behavior of flame spread downward over typical timber sheets and heat transfer analysis. Dissertation for Ph.D in University of Science and Technology of China, 2006.(in Chinese)

[4]Norton G A. A review of the derivative thermo-gravimetric technique (burning profile) for fuel combustion studies. Thermochimica Acta; 1993, Vol.214, pp.1-3.

[5]Liu Naian. Kinetic and analyse method of thermal decomposition of biomass. Dissertation for Ph.D in University of Science and Technology of China; 2000. (in Chinese)

[6]Guo, J., Lu, A. C. Kinetic study on pyrolytic process of oil-palm solid waste using two-step consecutive reaction model. Biomass and Bio-energy; 2001, Vol.20, pp.223-233. (in Chinese)

[7]Bilbao, R.. el a1. Kinetic study for the thermal decomposition of cellulose and pine sawdust in an air atmosphere. Journal of Ana1. Pyro1; 1997, Vol.39, pp.53-64.

[8]Susott, R.A. Thermal behavior of conifer needle extractives. Forest Sciences. 1980, Vol.26.

[9]Orfao, J. J. M., el a1. Pyrolysis kinetics of lingo-cellulosic materials-three independent reactions model. Fuel; 1999, Vol.78, pp.349-358.

[10]Hu zhurong. Thermal anlysis knitics. Science Process; 2001.(in Chinese)